FRITZ HABER

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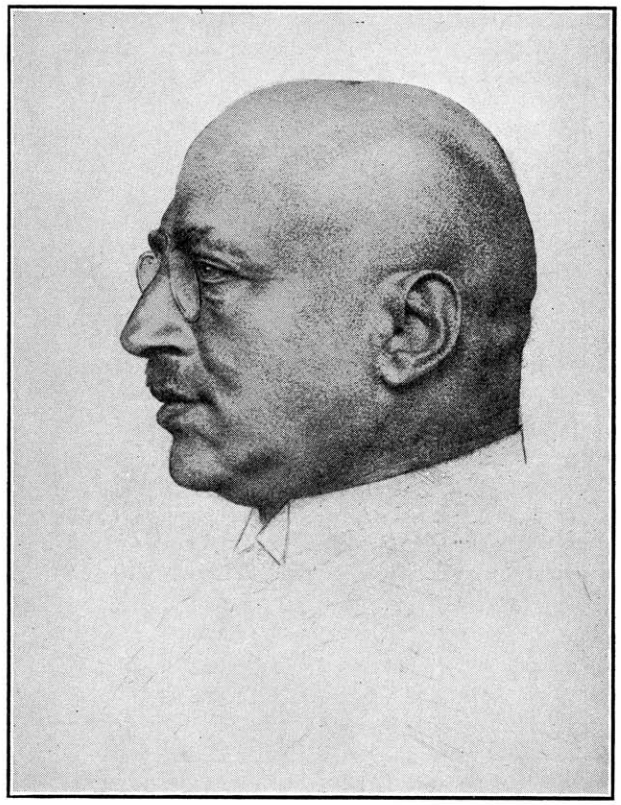
ON January 29, 1934, a great man passed from our midst. Fritz Haber was one of those men who made themselves immortal because of their life work—not only in the field of science, but also in the humanities. Haber created a world industry—that of synthetic ammonia. From this, other important, high-pressure industries sprang. The world production of synthetic ammonia for 1935 is estimated at nearly three million metric tons. Besides this great feat, Haber accomplished much other important and fundamental work, more than enough to leave to posterity a name of immortal fame.

Fritz Haber was born on December 9, 1868, in Breslau. He received his doctor's degree, with a dissertation in organic chemistry, under Liebermann who was co-inventor of synthetic alizarine. Haber did not work much in this field later on. Like so many famous men, he was an autodidact. Without being initiated by an older, prominent colleague, he carried out his great research work in the fields of electrochemistry, physical chemistry, technical chemistry, photochemistry, and physics. A decisive point in his life was that in 1894 when he came to Fritz Bunte at Karlsruhe. Bunte at that time and also later was active with Engler in the technical field, especially in the field of fuels. Haber accomplished an important part of his great and extensive research in Karlsruhe.

Wilhelm Ostwald classified scientists in two main groups (which, however, admit of some exceptions): scientists of the romantic type, such as Liebig, Gerhardt, and Alfred Werner who contributed greatly in their youth; scientists of the classical type, such as Faraday, Edison, Gibbs, and Helmholtz who carried out their great researches with almost unimpaired force and breadth of vision during the entire period of their long lives. It is difficult to put Haber in either of these classes. He did not achieve great works before his thirtieth year as most scientists of the romantic type seem to have done. Not until he had reached this age did the development of his personality begin in breadth and depth. In his habilitation thesis which he wrote at twenty-eight we find remarkable statements which are still interesting. Haber was among the first who studied the cracking processes which since have attained such importance. The decomposition of hexane and trimethylethylene by heat and the decomposition of illuminating gas on cooled surfaces were clarified by him. This and perhaps a few other researches he may have carried out at the instigation of Bunte. Soon after began an exceedingly important period, in which Haber was occupied intensively with electrochemical research. In 1898 appeared an introduction to these studies in his book "Grundriss der technischen Elektro-Chemie auf theoretischer Grundlage." Today this book is still of great interest. At that time it was believed that electrochemical processes in the field of oxidation and reduction chemistry would attain great industrial importance. However, the hopes which one had in this direction were only partially realized.



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The Faraday law, according to which 96,540 Coulombs per g.-equivalent are to be used for a substance to be transformed, destroyed these expectations somewhat. It is especially to Haber that we owe our enlightenment regarding the complicated processes of the reduction of aromatic nitro compounds in acid and alkaline media.

Engler, who besides his researches in oil, was occupied also with autoxidation problems, incited several valuable contributions of Haber in this particular field at the beginning of this century. Haber took up these again with more profound interest in

his later years. As happens so frequently, earlier researches formed the basis of later, fully developed scientific work.

From electrochemistry to pure physical chemistry was only a short step for Haber. Beginning with studies of gases, with which he was occupied about eight years previously, he studied gas equilibriums which shortly were destined to bring him to the peak of his scientific and technical attainments. Haber opened a new field in gas reactions, creating the pressure synthesis of ammonia—a monument to science which will outlive the centuries. It is known that the technical pressure synthesis opened a new scientific and technical field, the industrial importance of which cannot be estimated. In passing, it may be mentioned that one of the important uses of pressure synthesis, namely, the hydrogenation of solid and liquid fuels, had its origin also in Haber's Institute. At the time when Haber was occupied with his momentous research on the hydrogenation of nitrogen, Bergius was in Karlsruhe also. The writer ascribes it to this happy coincidence that Bergius conceived the important idea to apply pressure cracking hydrogenation upon solid and liquid fuels.

Haber, occupied with gas reactions, published in 1905 a book on "Thermodynamics of Technical Gas Reactions." This book was published at about the same time that Nernst advanced his third fundamental law of thermodynamics. In studying this important book, one is under the impression that Haber would have discovered the third fundamental law if Nernst had not anticipated him. About that time two Austrian industrialists, the Margulies brothers of Vienna, approached Haber, asking him if it was not possible to produce ammonia from nitrogen and hydrogen over nitrides and hydrides. This suggestion fell on fertile ground. Haber, with his collaborator G. van Oordt, studied the formation of ammonia from the elements. Like several scientists before him, such as Le Chatelier, Wilhelm Ostwald, Ramsay and Young, Perman and Atkinson, Haber determined the equilibrium between ammonia, nitrogen, and hydrogen at high temperatures of 1000°, without pressure. It is not generally known that several years previous to Haber's research work, Wilhelm Ostwald followed the same course, apparently with a good chance of success. By conducting nitrogen and hydrogen over technical iron, he obtained more than traces of ammonia. The tests which were carried out afterwards with iron, which was produced by reduction with hydrogen from iron ores, showed the error in Ostwald's experiments. The Ostwald iron yielded ammonia only as long as it contained nitrides. As soon as the nitrogen of the nitrides was transformed into ammonia, the effect of the iron at normal pressure became nil. The writer knows of a similar case, although of less industrial importance. Scientists asserted that carbon may be converted, without pressure, into methane if the carbon to be hydrogenated is precipitated upon nickel. The nickel acts as catalyst at the hydrogenation reaction. It could be shown, however, that methane was formed only so long as the nickel carbide which was present was converted with hydrogen into methane. If the carbide was decomposed, no further formation of methane took place.

Haber's research work with van Oordt regarding the production of ammonia from the elements was continued with LeRossignol. Their results did not concur with the calculations of Nernst, based upon his third fundamental law, which meanwhile had been published. A discussion started between these two great scholars, in which Nernst called attention to the fact that by increase of pressure the equilibrium of the exothermic nitrogen hydrogenation may be displaced in favor of a larger formation of ammonia. Historically considered, Nernst was the first who, with his collaborator Jost, produced ammonia from the elements at 50 atm. pressure with platinum, iron, and later on with manganese as catalyst at 685°C. Nernst seemed to realize fully the importance of pressure synthesis. According to a story which was told the writer some time ago, Nernst asked a leading German chemical industrialist, who died recently, if it were technically feasible to carry out a reaction at glowing heat and pressure of several hundred atmospheres. The answer was supposed to have been, "This is absolutely impossible." Haber, accustomed to carry out his ideas himself, did not consult a so-called expert, but with his collaborator, LeRossignol, built a small apparatus in which ammonia could be synthesized under pressure. Meanwhile it was found that the chemical constant of the hydrogen was not 2.2, according to Nernst's first estimation, but 1.6. Therefore, Haber's estimations for the NH_3 content in the equilibrium, which Nernst found to be much too high, was somewhat lower than it was established afterwards. Haber, who at first was rather pessimistic regarding the industrial value of the pressure synthesis of ammonia, changed his mind, and thus was opened the field of technical pressure-hydrogenation.

Haber's older colleague, Engler, was also a member of the board of directors of the Badische Anilin und Sodafabrik (now the I. G. Farbenindustrie—A. G.). This concern was interested at that time in nitrogen problems. Experiments were carried out to bind nitrogen of the air by combustion of air and by synthesis of nitrides. Engler aroused the interest of this firm, and Messrs. Bosch and Mittasch were sent to Karlsruhe to inspect the apparatus. It was shown to these gentlemen and, as usual in such cases, it did not function. However, the difficulties were met the same day. From that day on the development of pressure synthesis began. In an exemplary manner Haber not only carried out the thermodynamic investigations, but also invented the so-called circulating system, whereby, under pressure, the nitrogen-hydrogen mixture circulates continuously, fresh gas being added as the reactants are converted into ammonia. Everyone knows of the enormous task accomplished by Bosch with his collaborators, especially with Mittasch and Lappe, in order to overcome the technical difficulties of the process.

Haber proposed osmium as an excellent catalyst. It was established very soon that the world supply of osmium amounted only to a few kilograms and that one could not build up an industry on such a small quantity. The same was true of the uranium catalyst suggested by Haber. Not recalling that iron had been used before, Bosch suggested that experiments be made with it, supporting his suggestion with the remarkable reason that iron shows a complicated spectrum. The iron had to be produced directly from iron ore by reduction at comparatively low temperatures. Many experiments were carried out by Mittasch, of which a great many were negative, some satisfactory, and only a few showed good results. The best results were obtained with a Scandinavian iron ore, which was carefully analyzed. A considerable amount of alumina was found in it. Experiments proved the importance of admixture of alumina. Thus the so-called mixed catalysts, which afterwards played such an important part, were discovered. When Mittasch later on found time to occupy himself more intensively with the history of the catalysis, he and his collaborator, Theis, discovered that former scientists, especially Doebereiner, Magnus, Wöhler, Fand Mahla, and Deacon knew of the existence and importance of mixed catalysts, but that the knowledge of this group of substances had been completely lost.

Despite this fundamental research in the field of ammonia synthesis from its elements, Haber was not contented. He studied the so-called cold luminous arc and found that the formation of nitric oxide can be brought to high concentrations if sufficient ionization energy is added to the system. It may be assumed that this research work would have had important technical consequences if Haber had not invented and perfected the synthesis of ammonia from the elements which could be made on the greatest technical scale.

Before and during these important investigations Haber carried out other exceedingly valuable researches, partly in the field of gas chemistry, the coal element and the hydrogen-oxygen element. Haber recognized the Jaques coal element which was heralded widely to be a hydrogen-oxygen element. He destroyed the hopes which had been put in the direct electrochemical transformation of the coal energy into electric power. Furthermore, research was carried on in the following fields: beryllium compounds, production of aluminum, water gas equilibrium in the Bunsen flame, the theory of the speed of reaction in heterogeneous system, the principles of the separation of gases by centrifugal force, the anodic attack of iron by tram streams in the earth, the passivity of iron and the formation of surface layers, the reversible action of oxygen upon magnesium chloride and electric interfacial forces. One result of these important investigations is the glass electrode which has proved so valuable for pH measurements. Many of these investigations have become starting points for new research work.

All this important and basic research did not exhaust Haber's working power. He occupied himself with investigations regarding the escape of electrons from metals when they are transformed in oxides or salts. This research work was an important incentive for photochemical investigations carried out later on. Before the War he published important data on the optical analysis of gas mixtures and the development of the gas interferometer which carries his name and that of Dr. Löwe. Furthermore, papers were published on investigations regarding acoustic analysis of gases and the construction of the firedamp whistle. The latter contributions, especially the one on optical analysis of industrial gases, have become exceedingly valuable. Haber's conception of adsorption, which he attributed to the effect of radiating incompletely saturated attractive forces of the atoms in the space lattice, was of great consequence to further scientific research. According to his theory, molecular forces may be looked upon as being the effects of chemical valence forces, or, in other words, the effect of electromotive forces.

An important period in Haber's life was the World War. The writer knows from Haber's own lips how much he detested war and the horrors connected therewith. However, when this catastrophe occurred, Haber placed his services completely at the disposal of his people whose government, nineteen years later, rewarded him with base ingratitude. Haber was of the opinion, which is certainly correct, that the scientist in times of peace belongs to the world, but in times of war to his country. As early as November, 1914, the writer, who at that time was chief chemist of the Austrian War Ministry, came in contact with Haber. The Central Powers realized soon after the beginning of the War that the conflict would last much longer than Christmas, 1914, and that one had to prepare for a longer period. First it was necessary to produce great quantities of nitric acid—more than ninety-five per cent. of the total gun powder and explosives were based on nitric acid. It may be mentioned here that the Central Powers were not prepared for war. No measures had been taken to substitute nitrogen-oxygen compounds for Chile saltpeter, which was used exclusively at that time by the Central Powers. A small ammonia combustion plant was located in Gerthe near Bochum, Germany, and a still smaller air combustion plant was in Patsch near Innsbruck, Austria. Haber's first efforts were directed toward supplementing the amount of ammonia which could be obtained from coke oven plants. This was accomplished by increasing the production with the Haber-Bosch process and of calcium cyanamide. Ammonia obtained in this manner had to be transformed into nitric acid in ammonia combustion plants. The diluted acid had to be highly concentrated or converted into artificial saltpeter. To accomplish this required more than one year. The small amounts of saltpeter which were present in Germany and in Austria at the beginning of the War would certainly not have been sufficient to meet the demand. It may not be generally known that after the fall of Antwerp, fifty thousand tons of Chile saltpeter

were found in the storehouses along the harbor which became accessible to the Central Powers. If this supply of Chile saltpeter had not been there, or if it had been thrown into the River Schelde, the War, in the opinion of the writer, would have ended not later than Spring, 1915, on account of lack of explosives.

The second great achievement of Haber, who was frequently to be found in the front trenches, was in the organization of the gas war. Haber, later on, was reproached a great deal for it. However, if one accepts war as such, these reproaches certainly were not justified. It is beyond dispute that gas explosives, even though rather ineffective, were first used by the French army. Haber directed the measures for the chlorine gas attack which were temporarily successful at Ypres in the spring of 1915. Inasmuch as one had to depend on the direction and change of wind, the blow method was substituted later on with gas shells. Haber prepared not only for the offensive, but also for the defensive. Under his direction fundamental research work on gas mask protection was carried on. Gas masks, as well as gas war substances, have proven very valuable after the War, the latter especially for the destruction of vermin. From this it may be seen that what was originally planned for destruction turned out to be a blessing in the end.

After the War, Haber returned again to his beloved science—always with the thought to mitigate as much as possible the consequences of the War. It is known that he made thorough studies to determine if the enormous quantities of gold present in the oceans might not be recovered to pay Germany's war debt. After several years of intensive work, however, he had to discontinue this plan, since due to insufficient concentrations, the recovery of the gold in sea water would have been too expensive.

As early as before the War, Haber took over the direction of the Kaiser Wilhelm Institut for Physical Chemistry, which he made famous. Everybody knows that this institution attained world fame under his direction and through the excellent collaborators who gathered around him.

After the War, Haber broadened the base of his activities. He published important scientific articles regarding the most diversified fields. Above all this, he placed his services more and more at the disposal of his people. While before and during the War he published articles on investigations of ammonia equilibrium at normal and increased pressures and the determination of the heat formation of ammonia from its elements at different temperatures, after the War he carried out important research work on amorphous precipitations and crystallizing soles which resulted in the determination of the coalescence velocity and the rearrangement velocity. Combined with his research work regarding the presence of gold in sea water are his investigations on the production of artificial gold from mercury. The contributions of Miethe and Stammreich, which created a sensation, could not be disregarded, as it seemed possible that mercury with the atomic number 80 could be transformed into gold with the atomic number 79 by the splitting off of one electron. However, when besides gold, silver with the atomic number 47 could be detected in considerable quantities, it was clear that gold and silver were mere contaminations contained in the mercury used in other parts of the apparatus. This fact has been completely confirmed later on.

Among his last exceedingly important researches with his collaborators, the one on the mechanism of combustion and the radicals found in flames is especially remarkable. With Bonhoeffer he examined flames spectroscopically and found active hydrogen, hydroxyl, dicarbon, and methene. The conception of the chain reaction by Bodenstein in 1912–13 gave Haber the key to the explanation of the reaction in flames. The last years of his scientific work were devoted to the chain reactions. With Franck he recognized that the autoxidation of watery sulfite solutions represents a chain reaction started either by cupric ions, ultra-violet radiation, or oxidizing agents, whereby the radical SO_3 or monothionic acid, SO_3H, continues the reaction. Of fundamental importance are the investigations published with Willstätter on radicals in the chain-reaction mechanism of organic and enzymic processes. This permitted the classification of a large number of reactions under one heading. The contact substances (enzymic or ferric compounds) are reduced monovalently. The substratum in the starting reaction is oxidized monovalently. In the main reactions the dehydrogenation product—a radical—is formed which would indicate a valence loss with carbon, less frequently with oxygen. From this radical I another radical II is formed, aside from the end-product determined by the other reagents present. The monodesoxy enzyme or the ferro compound formed from the enzymic or the ferri compound is oxidized by oxygen or another oxidizing agent with or without the help of the substratum. Through repetition the main reactions I and II produce this chain which ends only if two similar or two dissimilar radicals disappear. Another way of breaking the chain is through the interaction of a radical with an inhibitor.

The catalysis of hydrogen peroxide through ferrous compounds is explained by the following chain reaction:

$$\begin{aligned} Fe_{II} + H_2O_2 &= Fe_{III}(OH) + OH \\ OH + H_2O_2 &= H_2O + O_2H \\ O_2H + H_2O_2 &= O_2 + H_2O + OH \\ Fe_{II} + OH &= Fe_{III}(OH) \end{aligned}$$

It cannot be foreseen what further consequence these last researches will have in the field of flames, explosions, synthesis, and enzymes.

Haber's activities did not end, however, with the accomplishment of great scientific research. After the War, when the pursuit of scientific studies seemed to languish in Germany because of inflation and other matters, it was he who created the "Notgemeinschaft der Deutschen Wissenschaft." This institution was exemplary and most beneficial. Advised by representatives of science and industry, a board of trustees functioned which supplied scientists with the means for carrying out research work on a large scale. This money

was supplied by the State. Valuable apparatus could be bought which, after having served at a certain place, was sent to other places where it was needed.

In the Kaiser Wilhelm Gesellschaft Haber's influence was of greatest importance. This Society established a great number of research institutes, of which the Kaiser Wilhelm Institut for Physical Chemistry was the first. The first president of the Kaiser Wilhelm Gesellschaft was the famous theologian Harnack, the grandson of Justus Liebig. The second president was Max Plank. When Harnack was asked what he did to make this organization famous, he answered, "I chose the most brilliant scholar in his field, and the Kaiser Wilhelm Gesellschaft built the Institute around him."

Haber was among the first who were successful in reëstablishing relations broken during the War with scientists of other countries. He deserves great credit for this. Just as he did his best during the War for the common good of his people, so after the War he was the first to recognize the international position of science and its representatives and made all efforts to tear down hampering barriers.

Haber was one of those few men in whom scientific creative power was united with wonderful ethical qualities. Anyone who came in contact with him was richer for it—he always gave, while the other received. The latter years of his life were sometimes aggravated by sickness, from which he partially recovered. His prophetic words spoken six years before his death and dedicated to Liebig, hold good for him.

> "And now he goes, filled with the thought and action of chemistry as its champion and hero, with slower-moving steps to the end of his life."

Haber was endowed with a great intellect. He was able to separate almost instantaneously and with unprecedented sagacity the essential and valuable from unimportant matters. He was a master of the written word. His treatises are distinguished by their clearness of description. His lectures are master works. His last academic lecture was given on request of the writer on the occasion of the Liebig-Wöhler celebration in Darmstadt in 1928. The real Haber certainly cannot be defined better than by his own words in which he portrayed Liebig in this wonderful lecture, and which really might be called Haber's autobiography.

> "We ask, before we take leave of him, after having said so much of his strength of will and mind, how was it with his soul? For no one deserves to be counted among the immortals—no matter how great his power, and inspired his mind—if he lacks greatness of soul. All who knew him say of him that he was true from the bottom of his heart, upright and good, yet proud and of high thoughts. . . . Friends tell of events which show that he was kind-hearted and helpful. But it seems to me that more than such characteristics of a man is the love which he has gained and which follows him beyond the grave. I know of none among the warriors of our science, yea in the whole field of natural science, who received more grateful love during his life and who had greater love follow him into eternity."